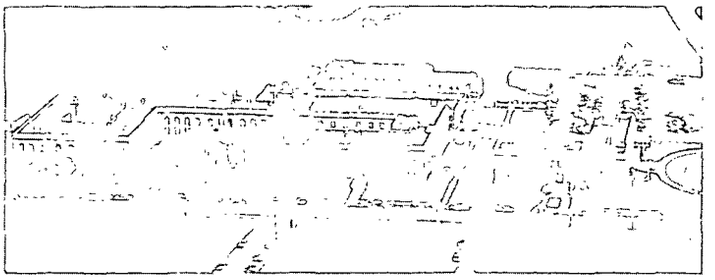

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

IPC TECHNICAL PAPER SERIES
NUMBER 32

STUDIES ON POLYMORPHY IN CELLULOSE. PART 2. CELLULOSE IV AND SOME EFFECTS OF TEMPERATURE

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MAY, 1976

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SUMMARY

As part of our program to explore the response of cellulose fibers to temperature, we have carried out some studies on the effects of temperature on regeneration from solution. We have found that regeneration at elevated temperatures results in significant variation in polymorphic form. In particular, the cellulose IV polymorph, heretofore prepared only from mercerized cellulose at temperatures above 180°C, has been regenerated from solutions in the 100-150°C range, and from two different solvent systems. At slightly higher temperatures (160-170°C), and for cellulose of sufficiently low molecular weight, the cellulose is recovered in the native (I) polymorph; the first such instance was reported by us in Science in 1974.

The effects of temperature on the structure of regenerated cellulose reflect the basic tendencies of unrestrained cellulose molecules. They provide important insights into the factors which control the response of pulp fibers to variation of process conditions in a wide range of production operations.

To be published in the Proceedings of the Symposium on "Conformation of Polysaccharides in the Solid State and in Solution," a centennial symposium of The American Chemical Society.

STUDIES ON POLYMORPHY IN CELLULOSE. PART 2: CELLULOSE IV AND SOME EFFECTS OF TEMPERATURE

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ABSTRACT

The supermolecular structure of cellulose precipitated from solution is quite sensitive to the temperature of regeneration and the degree of polymerization (DP). The effects of temperature have been explored in studies of regeneration from solutions in phosphoric acid as well as from solutions in the recently developed dimethylsulfoxide-paraformaldehyde (DMSO-PF) solvent system. When the celluloses are characterized by x-ray diffractometry the samples regenerated at or below room temperature appear predominantly of the cellulose II form. As the temperature of regeneration is elevated above room temperature increasing proportions of cellulose IV are indicated. At higher temperatures (100-150°C) the IV polymorph is the dominant form, the degree of order varying with DP and the time scale of the precipitation process. Ultimately at 160°C and for relatively low DP, the regenerated form is in the native or cellulose I polymorph. Raman spectral studies of the same samples show them all to contain varying proportions of cellulose molecules in the conformations typical of celluloses I and II. Conformation II is dominant in samples precipitated at or below room temperature. As the temperature of precipitation increases, a greater proportion of cellulose separates from solution in conformation I. In the samples precipitated above 100°C, which by x-ray diffractometry appear to be cellulose IV, the Raman spectra indicate similar proportions of conformations I and II. Thus these two conformations appear to form a mixed lattice in the cellulose IV polymorph.

INTRODUCTION

In the first of these studies of polymorphy in cellulose (1,2) it was proposed that cellulose chains in ordered regions can exist in either of two stable conformations, one of which is predominant in the native (I) form, the other in the mercerized or regenerated (II) form. It had also been established that regeneration of cellulose at elevated temperatures results in recovery in forms other than the cellulose II usually recovered by precipitation at room temperature (3). In the present report the effects of temperature on polymorphic form are examined in greater detail, and the results are interpreted in terms of the proposals concerning the two stable conformations of cellulose.

In the previous report (3) concerned with effects of temperature, attention was focussed on conditions which led to recovery of cellulose in the native lattice upon precipitation from solutions in phosphoric acid. The studies have been expanded to examine regeneration from phosphoric acid under other conditions, as well as regeneration from the recently developed dimethylsulfoxide-paraformaldehyde (DMSO-PF) solvent system (4).

EXPERIMENTAL

Regeneration from phosphoric acid has been explored under a variety of conditions and for a number of different celluloses. The results presented here are confined to solutions prepared with Whatman CF-1 powder, shown by microscopic examination to consist of fragments of cotton fibers; viscosity measurements indicate a DP of approxiately 600. Experiments on regeneration from the DMSO-PF system (4) were carried out entirely on the CF-1 powder. The regeneration procedures will be set forth in some detail as previous reports have led to a number of requests for more complete descriptions.

REGENERATION FROM H_3PO_4

Two series of regenerations were carried out with this system: (a) a series based on regeneration at different temperatures after relatively short aging of the solutions, and (b) a series based on regeneration at different temperatures after aging of the solutions for three to four weeks in order to reduce the DP.

Solutions

Approximately 10 grams of cellulose powder were wet with 7 grams of water and allowed to equilibrate for an hour; 330 grams of 85% phosphoric acid were stirred in a little at a time. The solutions were stored away from strong light for the appropriate period with occasional stirring. They were filtered through "F" glass filters prior to regeneration.

Regeneration

350 Ml of glycerol were saturated with prepurified nitrogen in an open three neck flask fitted with a mechanically driven agitator and a thermometer. The temperature was raised to the value chosen for regeneration and maintained during the precipitation. The solution, also nitrogen protected, was added in a small stream, near the continuously bubbling nitrogen, over a 25 minute period. Stirring at the temperature was continued for 10 minutes, then 800 ml of boiling water were added, very cautiously at first, and eventually fast enough to complete the addition in 5 minutes. The precipitate, now at approximately 100°C, was centrifuge washed with near boiling distilled water. The washing was repeated 5 times, the third wash including pH adjustment with aqueous ammonia. After the final wash the precipitate was freeze dried.

DMSO-PF

Regeneration from the DMSO-PF system was confined to the undegraded Whatman CF-1 powder. Studies by Swenson (5) have established the nondegrading nature of this solvent system.

Solutions

Since activity of this solvent system is inhibited by moisture the cellulose powder and the paraformaldehyde were first dried in a vacuum oven and the DMSO was dried over molecular sieve. Fifteen grams of cellulose in 500 ml of DMSO were heated to 120°C in a closed container fitted with a stirrer and condenser. At 120°C four to five grams of PF were added. Rapid decomposition of the PF was followed by dissolution of the cellulose to give a clear viscous liquid.

Regeneration

Precipitation of the cellulose from the DMSO-PF solvent system was carried out by addition of the solution in a dropwise manner to the precipitating medium at the temperature of interest. The media were as follows: -2°C, 1:15 methanol-water; 20°C, water; 60°C, water; 100°C, water; 127-130°C, 1:9 water-glycerol under N_2; 165-170°C, glycerol under N_2. Needless to say, at the higher temperatures caution is exercised. The precipitated cellulose was then washed and freeze dried.

CHARACTERIZATION

The samples were characterized by x-ray diffractometry and Raman spectroscopy. The freeze dried powders were pressed into pellets at approximately 2000 psi for this purpose. Some of the pellets pressed for x-ray diffractometry had TiO_2 added as an internal standard.

The x-ray scattering measurements were made with a Norelco diffractometer utilizing nickel filtered copper K-α radiation in the reflecting mode. The

Raman spectra were recorded on a Spex Raman system using the 5145 A line of a coherent radiation 52-A (Argon) laser for excitation. The spectra were recorded using the backscattering (180°) mode. In most instances the laser-excited fluorescence (6) decayed to acceptable levels in approximately 30 minutes. Some of the samples regenerated from H_3PO_4 at elevated temperatures were bleached in chlorine dioxide prior to freeze drying and subsequent characterization; it has been established that this bleaching procedure does not in any way influence polymorphic form.

RESULTS

The diversity of polymorphic forms induced by the variation in temperatures is reflected in the x-ray diffractograms of the precipitated celluloses. Figure 1 shows the diffractograms of the celluloses precipitated from the DMSO-PF system. The diffractograms for the series regenerated from H_3PO_4 after aging of the solutions for periods less than one week indicate essentially the same range of polymorphic variation. Comparison of these diffractograms with published diffractograms for the different polymorphic forms (7,8) indicate that the samples precipitated at the lower temperatures are essentially in the cellulose II form. As the temperature of regeneration is increased (20 and 60°C) the celluloses become more crystalline, though the form remains clearly a cellulose II. The first departure from this pattern is noted at 100°C where the (002) peak becomes the most intense feature, and indications of a new feature in the 14-16° region appear. At 127-130°C the diffractogram is typical of low crystallinity cellulose IV, and at 165-170°C, it is clearly a cellulose IV diffractogram.

The diffractograms in Fig. 2, which were recorded for the celluloses regenerated from phosphoric acid after aging for three to four weeks, show an even wider range of polymorphic variation over approximately the same temperature

range. At room temperature a highly crystalline cellulose II is formed. At 100°C, substantial conversion to the IV form is noted, although a residual amount of the II form is also indicated. The features characteristic of the II form are further diminished at 120°C and are essentially eliminated at 140°C. At 140°C, however, the feature at approximtely 16° possesses a somewhat complex structure, perhaps suggestive of the beginnings of its resolution into two distinct peaks as clearly occurs at 160°C, where the diffractogram is typical of a high crystallinity cellulose I. The recovery of the cellulose in the I lattice under these conditions has been reported elsewhere (3).

The Raman spectra of the series of regenerated samples represented in Figs. 1 and 2 are shown, respectively, in Figs. 3 and 4. Though the spectra reflect the variation in polymorphic forms, the pattern of the spectral changes does not provide a simple correlation with the x-ray diffractometric indices of polymorphic form. In order to place the Raman spectra of the present samples in perspective x-ray diffractograms and Raman spectra of a series of celluloses mercerized to varying degrees (9) are reproduced in Figs. 5 and 6. The diffractograms in Fig. 5 are consistent with prior observations on systems of this type (8). The Raman spectra of similar partially converted samples have been reported and discussed previously (2). The essential pattern of variation in these spectra is that, particularly in the low frequency region ($<600\ cm^{-1}$), cellulose I and cellulose II have distinctly different spectra. The partially converted samples have spectra with features which occur in the spectra of both the I and II polymorphs.

The most remarkable observation revealed in a comparison of Fig. 3, 4, and 6, is that the spectra of samples which produce distinct cellulose IV diffractograms are essentially similar in most respects to the spectra of the partially converted celluloses which are mixtures of the I and II polymorphs as

indicated in the diffractograms in Fig. 5. Indeed this observation is representative of many others wherein spectra of cellulose IV samples appear almost identical to the spectra of the mixed I and II samples obtained by incomplete mercerization. The differences which do occur are usually of the type which arise from variations in the degree of crystallinity.

It should perhaps be noted that although the primary determinant of polymorphic form appears to be the temperature of regeneration, both the DP of the cellulose and the mechanics of the regeneration process are important factors. It is generally true that the lower the DP the higher the degree of order measured in terms of the width-at-half-height of the peaks in the diffractograms. This effect of low DP appears to be operative under all conditions of regeneration.

The effects of regeneration mechanics, though somewhat more complex, are perhaps best characterized in terms of the time allowed for separation from solution. For example, the regeneration from the DMSO-PF system by the procedure described above gave a cellulose of low order at 127-130°C. In contrast, in a related experiment wherein the solution was held at 135°C until the cellulose separated due to the slow thermal dissociation of the methylol substituent the precipitated cellulose was more ordered, as indicated by the diffractogram shown in Fig. 7 which is typical of highly ordered cellulose IV samples.

In this connection it should also be noted that preparation of cellulose IV by regeneration from solution is novel. Previous reports of its preparation have been based on treatment of celluloses I or II at temperatures in the range 180-250°C in glycerol (7).

DISCUSSION

The first investigation in this series of studies on polymorphy in cellulose focussed on interpretation of the differences between the Raman spectra of celluloses I and II. Comparison of the differences with the spectra of model compounds, and a theoretical analysis of the influence of conformation on vibrational spectra, led to the proposal that the cellulose chains possess different conformations in the two polymorphic forms. Taken together with published mappings of the potential energy (10) and the constraint of a repeat distance of approximately 5.15 A per anhydroglucose unit, the spectra suggested that only two conformations of the cellulose chain are likely to be stable. These have been represented as relatively small left- and right-handed departures from the twofold helix structure. For convenience in the discussion of other polymorphs the two conformations have been identified with the polymorphs in which they are predominant. Thus conformation I is the one dominant in native cellulose while II is the conformation in the mercerized form.

It was noted in (2) that the interpretation set forth in terms of only two stable conformations required, for consistency, that the other polymorphic forms be constituted of these same two conformations. The spectra of the cellulose IV samples shown in Fig. 3 and 4 are in accord with this requirement for, as noted above, they appear to be superimpositions of the spectra of forms I and II. Since this observation is true of many different samples of celluose IV prepared in the course of these studies it seems clear that conformations I and II coexist in the cellulose IV polymorph. When the distinctive x-ray diffractograms of the cellulose IV samples are considered as well, the only interpretation that remains plausible is that the cellulose IV polymorph represents a mixed crystalline habit in which both conformations coexist.

Though the effects of temperature are in part modified by the mechanics of regeneration and the DP of the cellulose, certain clear patterns emerge. The most obvious feature is that as the temperature of regeneration is raised above a certain level, which is determined in part by DP, an increasing proportion of the cellulose chains separate in the I conformation. These seem to coprecipitate with molecular chains separating in the II conformation, giving rise to a fraction of the total precipitate in the IV form, while the majority of the precipitate remains the II polymorph; thus, for example, the 100°C sample in Fig. 1 and 3. As the temperature is increased further, or the DP lowered, a much larger proportion of the molecular chains separate as a coprecipitate of conformations I and II in the IV polymorph; thus for example the 127-130°C sample in Fig. 1 and 3 and the 100°C sample in Fig. 2 and 4. At higher temperatures still, for example the 165-170°C sample in Fig. 1 and 3 and the 140°C sample in Fig. 2 and 4, the IV polymorph dominates and there is no evidence for separate precipitation of the II polymorph. Ultimately, for a low enough DP and 160°C the molecular chains separate entirely in the I conformation and the crystalline form is that of the native cellulose I state, Fig. 2 and 4.

The interpretation set forth above for the present observations concerning the preparation of cellulose IV by precipitation from solution can also be reconciled with the results of past preparations of cellulose IV. The best established procedures previously reported (7,11) are based on treatment of cellulose II in glycerol or water under pressure at temperatures in the range 180-250°C. When this temperature range is compared with results concerning the glass transition temperature of cellulose (12), as well as the possible plasticizing effects of glycerol (13), it is apparent that the conditions prerequisite for formation of cellulose IV by direct transformation of cellulose II are precisely those which promote conformational mobility. It would seem, therefore, quite likely that a change in conformation is involved in this transformation. Studies

of some effects of temperature on mercerization of cellulose (9) appear to confirm this interpretation.

The effect of DP on crystalline form has already been noted above. In Fig. 2 it is clear that the lower DP of the samples aged for 3 to 4 weeks in H_3PO_4 has led to initiation of the conversion to conformation I at lower temperatures, in addition to generally resulting in more ordered precipitates. Ultimately the regeneration in the cellulose I form has so far been possible only for the low DP samples. This may reflect an inherent limitation on the nature of the I conformation, though this possibility has not yet been fully explored.

The influence of time is not unrelated to the effects of DP. In general it appears that for samples of high DP it is necessary that they be held for longer periods under conditions of high molecular mobility if a highly ordered structure is desired; thus the contrast between the 127-130°C sample in Fig. 1, where the precipitation from the DMSO-PF system was rapid, and the sample in Fig. 7, where the separation from solution was much slower. The DP was the same in both instances.

CONCLUSIONS

A number of interrelated conclusions have been developed from the present studies. The Raman spectra of celluloses recovered under a wide range of conditions show features characteristic of one or the other or both conformations identified with celluloses I and II, and thus are consistent with the proposal that only two conformations of the chain are stable in ordered domains in cellulose. The spectra of the cellulose IV samples, when taken together with the distinctive x-ray diffractograms, suggest that the IV polymorph is a mixed lattice in which conformations I and II coexist.

Elevation of the temperature of regeneration appears to promote conversion of cellulose chains from the II conformation to the I conformation, the degree of conversion depending on the DP and, to a less clearly defined extent, on the mechanics of the regeneration process. In general, a lower DP permits greater conversion from the II to the I forms; the mechanics of regeneration become important when the time interval allowed for molecular ordering is limited.

On the basis of the above interpretations of the present observations it has been possible to design procedures for the regeneration of cellulose IV under a far wider range of conditions than heretofore reported.

ACKNOWLEDGMENTS

The authors wish to acknowledge many valuable discussions with Dr. Kyle Ward. Ms. Rebecca Whitmore assisted in some of the experimental phases of the work. Support from institutional funds of The Institute of Paper Chemistry is gratefully acknowledged.

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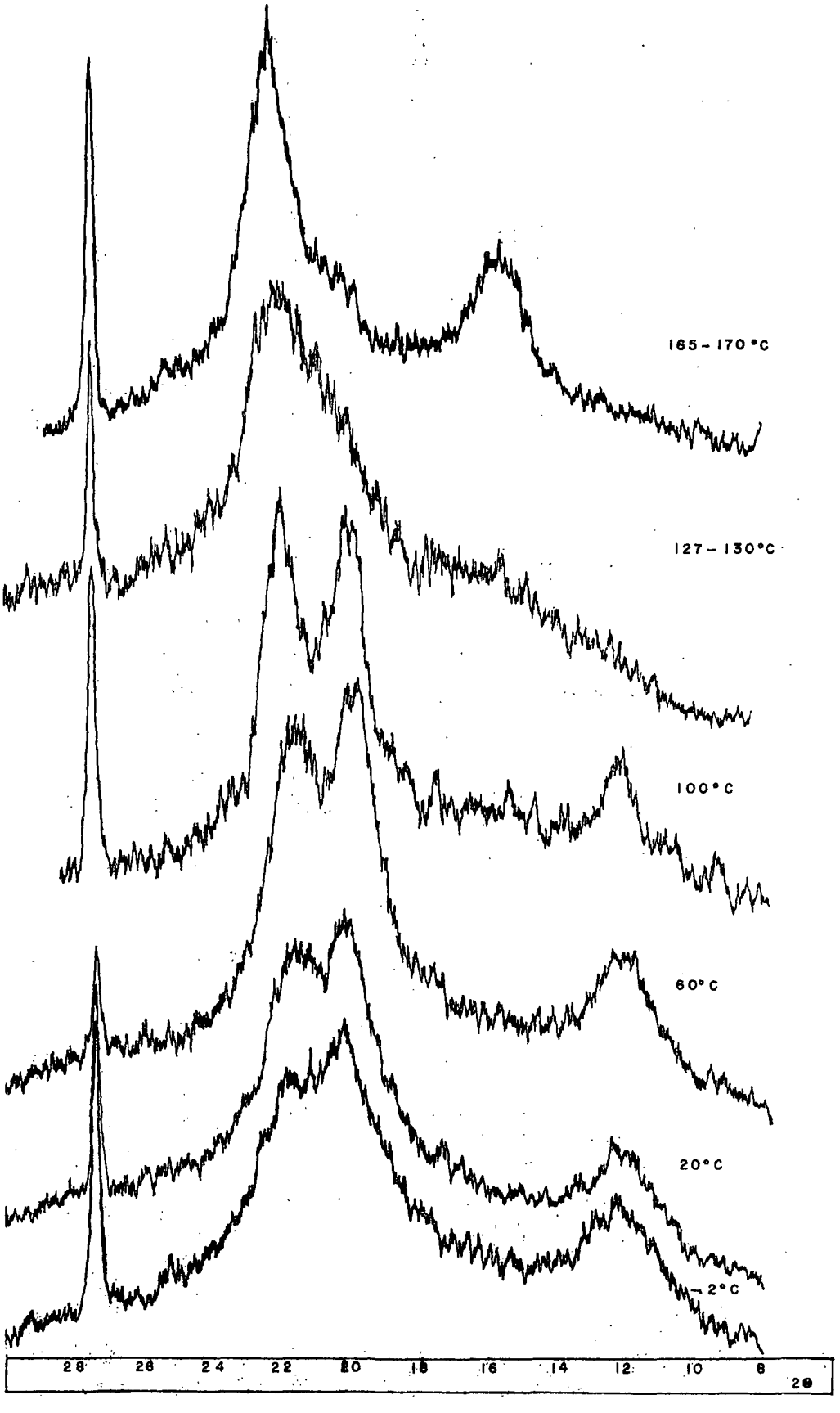

Figure 1. X-ray diffractograms of celluloses regenerated from the DMSO-PF system (the peak above $2\theta = 27°$ is due to TiO_2).

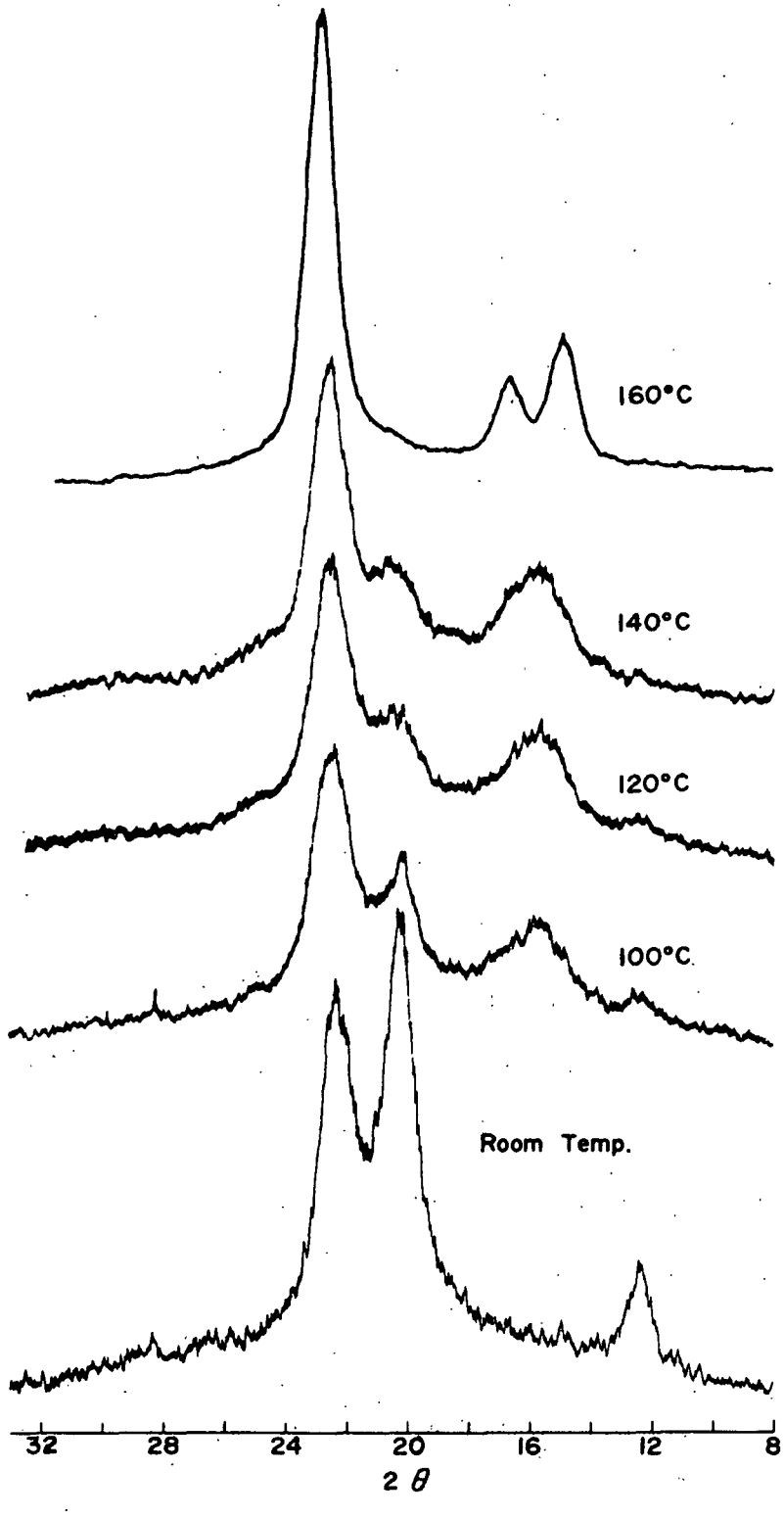

Figure 2. X-ray diffractograms of low DP celluloses regenerated from phosphoric acid.

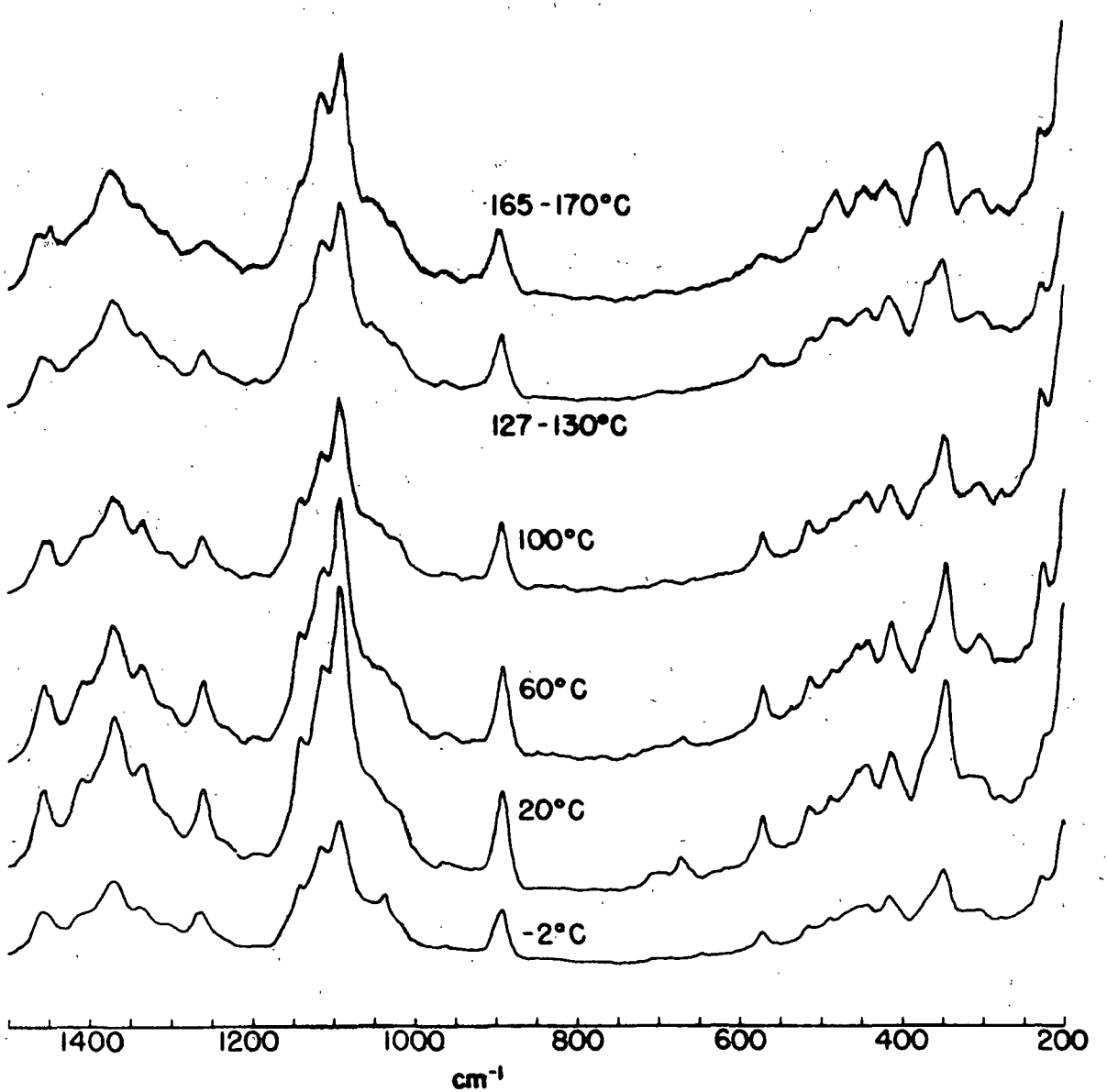

Figure 3. Raman spectra of samples identified in Figure 1.

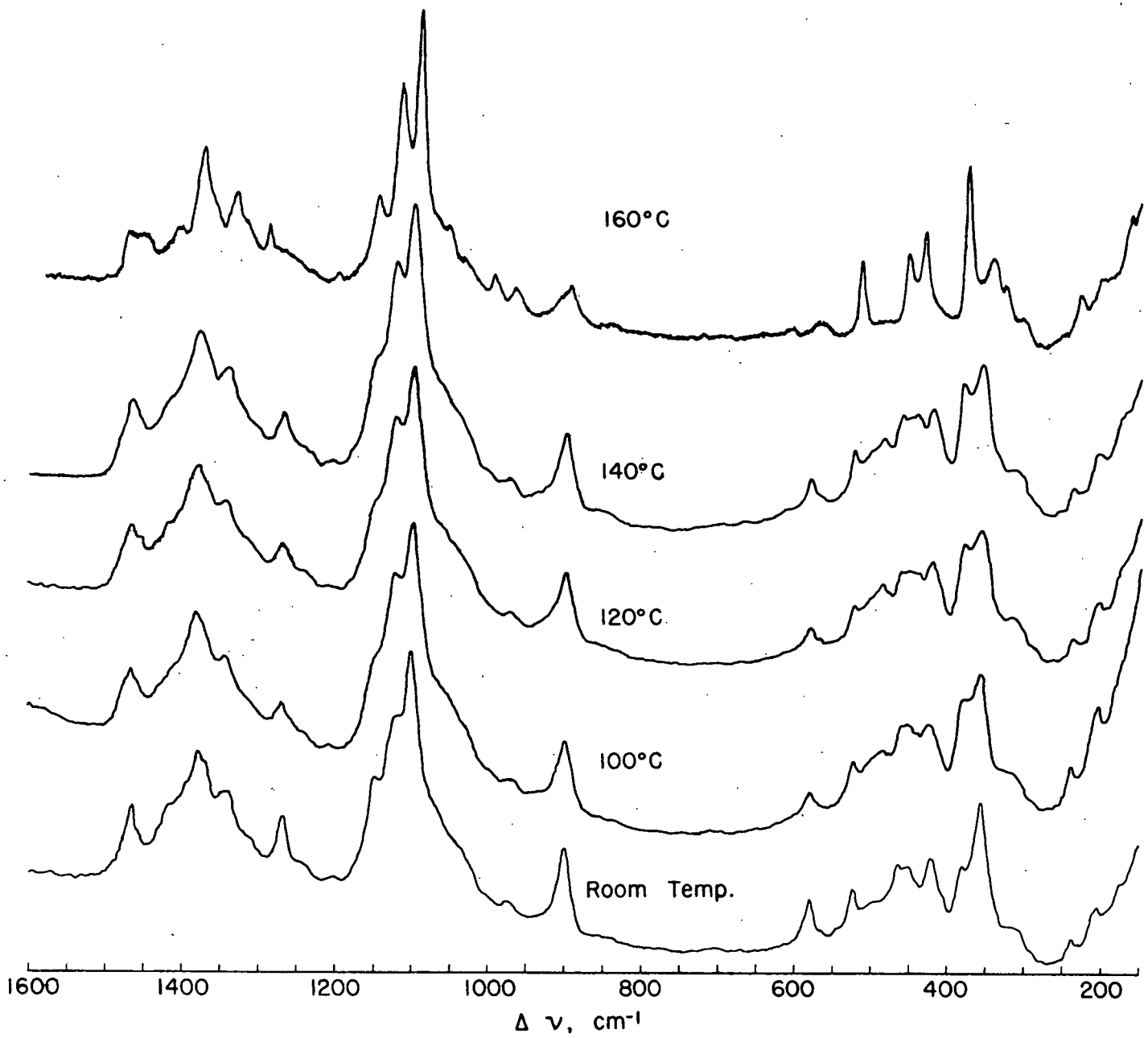

Figure 4. Raman spectra of samples identified in Figure 2.

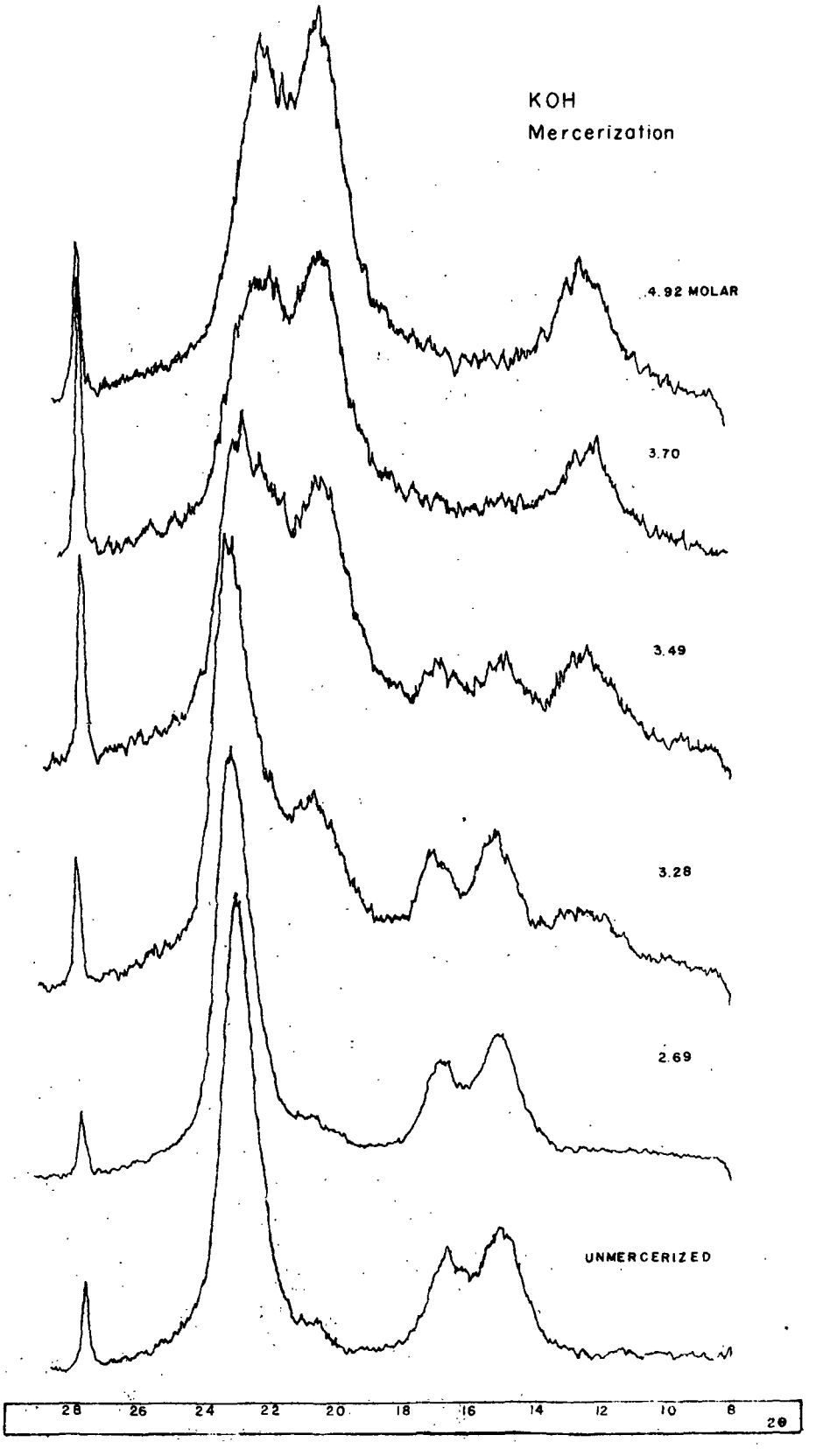

Figure 5. X-ray diffractogram of celluloses mercerized to different degrees.

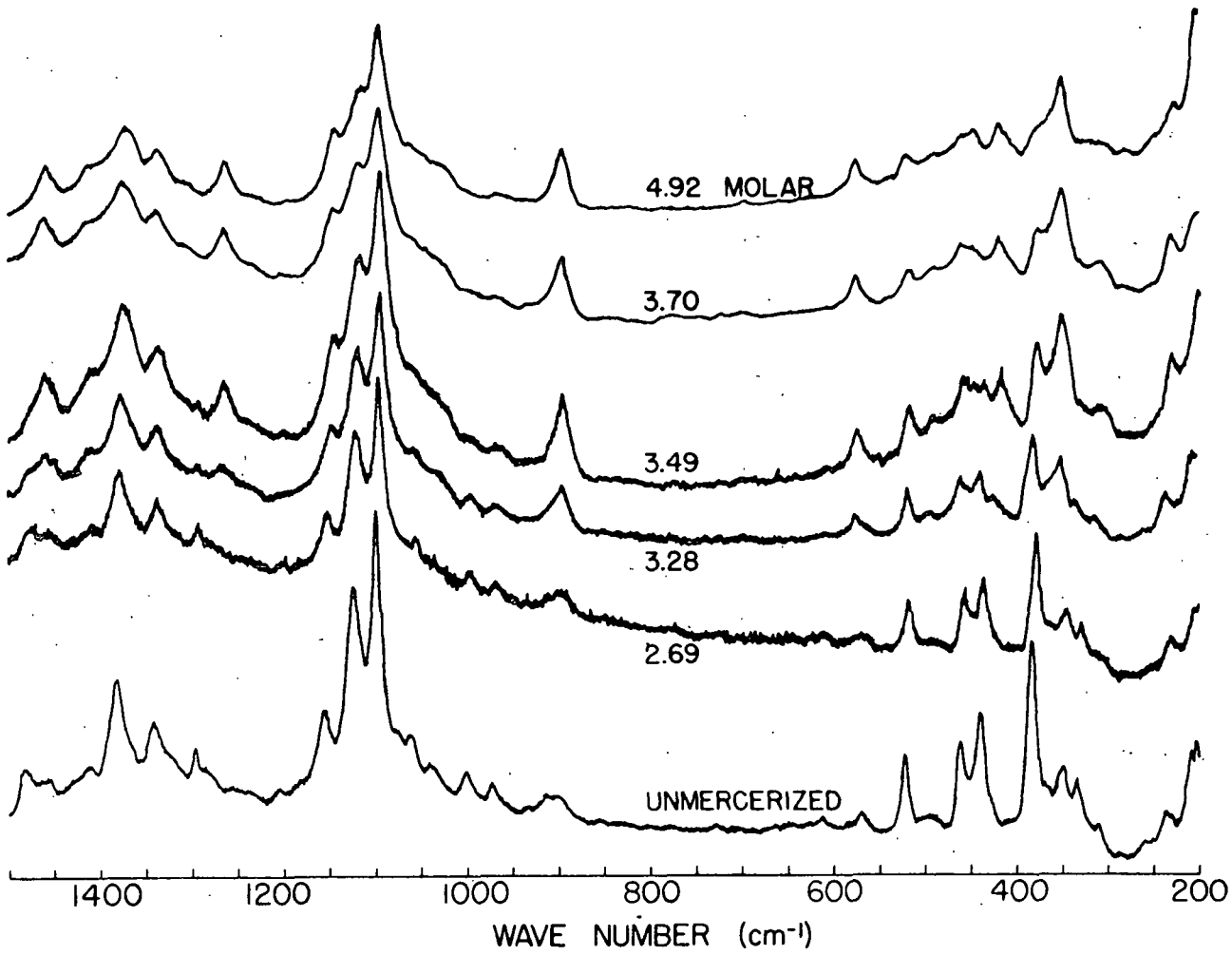

Figure 6. Raman spectra of samples identified in Figure 5.

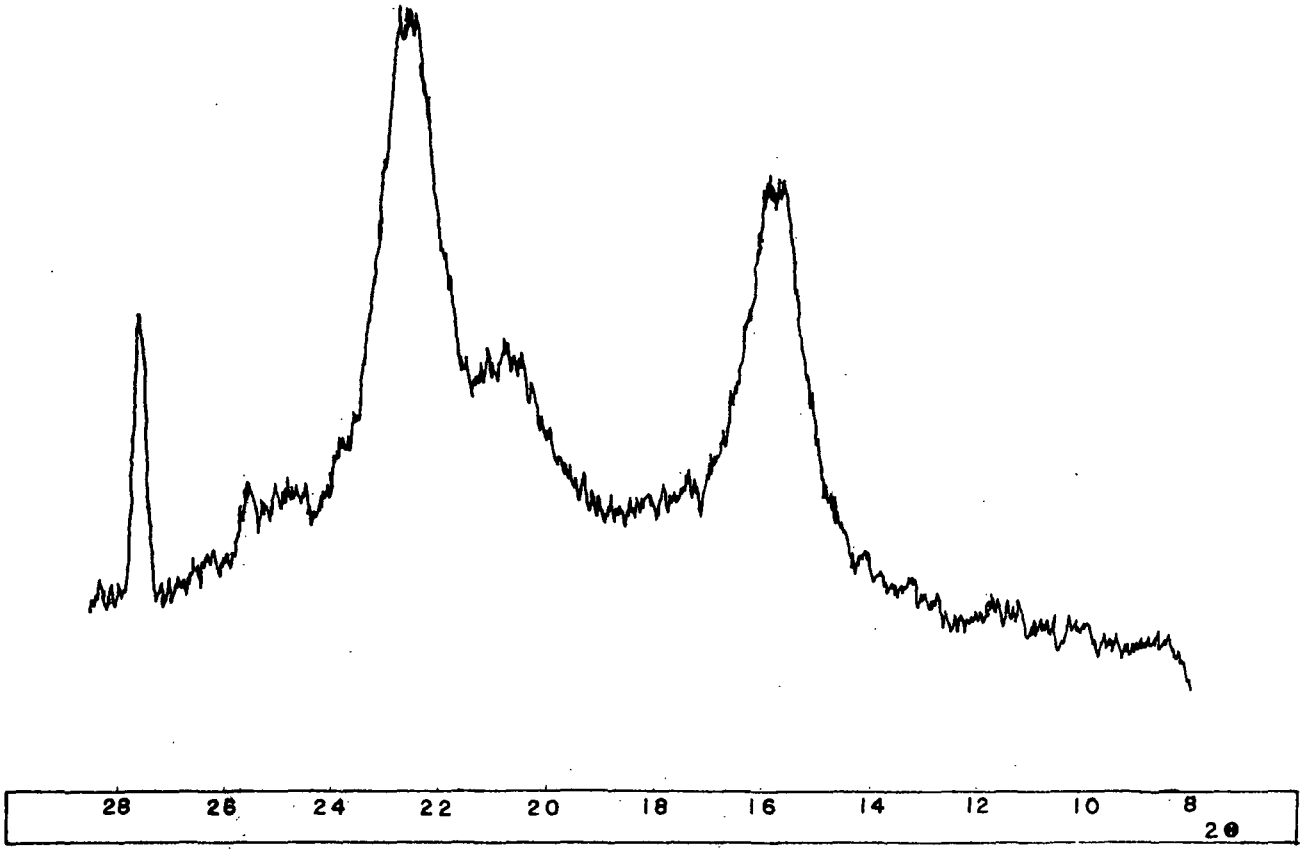

Figure 7. X-ray diffractogram of sample regenerated from DMSO-PF by slow precipitation at 135°C.